PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Improvements in or relating to Metallic Analysis

We, HOESCH AKTIENGESELLSCHAFT, of Eberhardstrasse 12, Dortmund, Germany, a German Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to an apparatus for determining the activity, particularly of oxygen, in metal baths.

In recent times, it has become necessary to break away from conventional methods for determining elements, particularly oxygen, in metal baths. In particular, the oxygen determinations previously used leave much to be desired, since these determinations (like the corresponding determinations of other elements) require excessively long times in relation to the progress of melting operations. Particularly in ascertaining oxygen content, the time required for the determination lessens the probability value of the determination, since the oxygen content of metallic baths changes rapidly. Moreover, the accuracy of known analytical methods is quite unsatisfactory with small amounts.

Attempts to find a determination method which is independent of time, particularly for determining the instantaneous oxygen content of metal baths, especially in the molten metal, has led to the introduction of electro-chemical activity determination. The determination of activities in aqueous solutions by means of an electrolytic circuit has been known for a long time. By a stratagem, it is possible to carry out corresponding determinations in metal baths, by making the molten metal the electrode, in which is immersed a high temperature-resistant electrolyte in contact with a comparison electrode which actuates a potential measuring instrument which is short-circuited with the metal bath. The determination particularly of oxygen content of the molten metal, for example steel, especially in technical metal baths, principally fails in that sources of error are provided by the gas phase disposed above the molten metal and, possibly, also the slag covering the molten metal influencing the measuring results.

Attempts have therefore been made to meet this requirement by embedding the electrolyte in a ceramic sleeve surrounding the covering surface of the electrolyte. The forms of electrolyte which have been used previously, especially for ordinary technical use, have not proved to be suitable. As a general rule, the electrolyte has the form of an immersible hollow cylinder, i.e. closed at the immersible end, receiving the comparison electrode. Such hollow cylinders do not withstand the sudden temperature change, especially if they consist of a housing of temperature-resistant zirconium dioxide, which is inherent in immersion of the electrolyte into the melt with instantaneous measurements. It has therefore been attempted to reduce the sensitivity to thermal shock of these hollow cylinders by covering the enclosed hollow cylinder of gas-impermeable zirconium dioxide constituting the electrolyte on both sides with a layer of gas-permeable zirconium dioxide. The manufacture of such electrolytes is very complicated and correspondingly expensive, since the sensitivity required by the basic shape of the electrolyte remains and, if need be, is reduced within certain limit. In particular, the use of such electrolytes in connection with hollow measuring heads, namely measuring heads for single determinations only, is economically not acceptable.

The invention is based upon the object of providing a measuring device which avoids the risk of erroneous measuring results and which is so cheap in construction on the one

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hand and so robust on the other that its introduction into technology, particularly its use for the continuous supervision of the Frisch process in the production of steel, is possible and economically allowable, even when it is connected with a device for only one determination.

A device taking into account this requirement must include an electrolyte, which can be readily manufactured and is, at the same time, resistant to mechanical and thermal stresses, as well as to undesired effects of other phases than the actual measuring phase and as a rule the molten metal, providing adequate screening of the electrolyte.

The invention accordingly consists in a device for determining the activity particularly of oxygen in metal baths, in which the molten metal represents one electrode, in which a high temperature-resistant electrolyte provided with a screen for eliminating outside effects is immersed in contact with a comparison electrode, which actuates a voltage measuring device which is short-circuited with the molten metal, in which a plug-shaped electrolyte is located in a temperature-resistant non-conducting carrier tube so as to project from and outwardly seal the carrier tube, to which is connected to a contact wire which is inserted into the carrier tube from above and which, together with an oxygen-containing medium which is gaseous at the measuring temperature and is introduced into the carrier tube, serves as the comparison electrode.

In contrast to the previously known devices, this device fulfils in a desired way the requirements which such a device must have for ordinary technical use. The compact electrolyte is sufficiently resistant to the mechanical stresses and, in particular, also to the thermal stresses necessarily connected with immersion in the metal bath. It is likewise manufacturable comparatively readily and consequently economically. The carrier tube on which the electrolyte is mounted serves both for supporting the electrolyte and screening it. Separate insulation is consequently no longer necessary.

Various embodiments of electrolytes and the carrier tubes surrounding them are possible. In the selection of suitable materials and also of their form, account is to be taken of the stresses likely to occur, particularly through the sudden changes of temperature. A material which is particularly suitable for the carrier tube is quartz, which is insensitive to thermal shock.

For commercial use, a device has proved to be suitable which is provided with a conically-tapering carrier tube, i.e. in the direction of immersion, in which the electrolyte is held in its end position in the form of a conical plug under spring pressure. It is naturally also possible to cast the electrolyte into the carrier tube. For this, it is desirable to roughen or groove the internal walls of the carrier tube. Particularly in the use of electrolyte materials with a high coefficient of expansion relative to the carrier tube, a construction has proved to be suitable in which a tapering carrier tube and a plug embedded in temperature-resistant material and carried on the inturned edge of the tube, with sufficient clearance in the tube, is provided with a projection projecting from the tube. Advantageously, the plug is made substantially spherical.

The comparison electrode, which must be in direct contact with the electrolyte, is formed by a wire of conductive, high heat-resistant and chemically-resistant material providing the connection between the electrolyte and the potential measuring device, for example a platinum wire, in connection with an oxygen carrier of constant oxygen partial pressure which is fluid or gaseous at the measuring temperature. The gaseous oxygen carrier passes preferably through the carrier tube surrounding and sealing the electrolyte as a scavenging medium. If the carrier tube is a cylindrical tube, from which the electrolyte projects at the immersion end, and the gaseous medium forming the comparison electrode together with the contact wire is passed through the opposite end, it is necessary for satisfactory measurement for the gaseous medium to be passed into the carrier tube through a supply duct extending to the base of the carrier tube, so that the gas supplied reaches the electrolyte arranged at the base of the carrier tube. Preferably, the carrier tube concentrically surrounds the supply duct and the contact wire is passed through the duct.

A special construction of the device according to the invention, dispensing with the supply duct, uses as the carrier tube a U-tube in which a contact wire is inserted which forms the comparison electrolyte in conjunction with a gaseous medium supplied to the U-tube, which wire is connected with a plug-like electrolyte projecting a limited amount from the U-tube, through an aperture in the base of the U-tube. Introduction of the gaseous medium forming the comparison electrode together with the contact wire proceeds more simply than in the substantially cylindrical tube proposed initially, which has to have a duct for the gas supply also provided. The wall of the U-tube opposite the aperture in the U-tube receiving the plug consisting of the electrolyte material satisfactorily forms a support for the plug inserted into the aperture, securement of the plug by special means therefore being no longer necessary.

The plug can be made conical so as to be located firmly in the aperture or it can also be supported against the internal wall of the U-tube with a member projecting from the aperture. Firm seating of the plug in the U-tube can otherwise be provided by reshaping the U-tube or by locking the plug in the U-

tube. It is also possible to insert into an initially cylindrical tube a plug adapted to the internal diameter of the tube and then to bend the tube into the desired U-shape. The tube can be made up with two portions receiving the plug between them, which are then fused to one another and to the plug to form a single unit.

For commercial use, it is necessary for the parts of the device which, as a general rule, must be changed after each measurement, that is to say, the electrolyte and the protective tube, to be readily and simply installable and also demountable. This aim is provided for in the further development of the invention in such a way that the carrier tube with the electrolyte located therein is embedded in known manner in an interchangeable connecting portion locatable on a measuring probe, lance or the like. The connection between the electrolyte and the constituents of the contact wire forming the comparison electrode can be provided by means of a clamp or plug-and-socket connector. In a preferred construction, the connection is provided by the twisted ends of the contact wire being inserted in a central aperture provided in the electrolyte. For twisting together the ends of the lead, a ceramic two-hole insulator block is preferably used. This kind of connection prevents any contact of the comparison electrode with the carrier tube.

In the use of a U-tube as the carrier tube, between the electrolyte and the contact wire, a plug-and-socket or like connection can be provided by securing the contact wire to the plug before shaping the carrier tube or before fixing the electrolyte plug into the carrier tube. However, the plug can also be provided with a boring, preferably extending into the base of the tube, in which the preferably twisted ends of the contact wire are inserted. An aperture in the plug can be provided at the same time in a plug otherwise closing off the cross-section of the tube, for the passage of the gaseous medium.

It is naturally also possible to combine the carrier tube, electrolyte and comparison electrode in a hollow head member extending from the measuring probe. The oxygen carrier forming one component of the comparison electrode can thus be cast in the hollow head. The short-circuit contact to the bath for the potential measuring device can also be connected in the hollow head. In this case, a clamp connection for the junction of the comparison electrode and that of the short-circuit contact is provided. Naturally, this does not close off the tube supplying a gaseous oxygen carrier through the measuring probe from the outside. In this case, the necessary leads are provided in the dip head and connections for the supply of the gas are provided on the head and on the probe.

The short-circuit contact can naturally also be inserted separately in the metal bath. Moreover, it is also possible to short circuit the potential measuring device with the metal bath by providing an auxiliary magnet on the container holding the molten metal, for example a casting mould, which magnet is conductively connected with the potential measuring device.

For the case where the electrolyte must be inserted through a slag cover or layer into the metal bath, a meltable sleeve screening the free end of the electrolyte or the whole dip apparatus can be provided, which ensures that the contacts, especially of the electrolyte, come against the molten metal exclusively.

In order that the invention may be readily understood, embodiments of it are described below, by way of illustration only, in conjunction with the accompanying diagrammatic drawings, in which:

Fig. 1 shows one form of the device according to the invention in vertical section;

Fig. 2 shows a fragmentary view of the dip head of Fig. 1 on an enlarged scale;

Fig. 3 shows an embodiment of the electrolyte with the carrier tube;

Figs. 4*a*, 4*b* and 5 show further embodiments of the electrolyte with the carrier tube;

Fig. 6 shows an embodiment using a U-tube as the carrier tube, in which is located the component of the dip head including the oxygen carrier;

Fig. 7 shows a further form of device according to the invention.

Referring to Fig. 1, a metallurgical vessel is indicated at 19, in which a molten metal 21 is located and is covered with a layer of slag 22.

Into the molten metal 21, there is inserted an electrolyte 13, for example consisting of ZrO_2 stabilised with CaO, which is held and guided in a protective tube 12 projecting it from the slag 22 and the atmosphere above the melt 21, 22, the tube 12 being screwed into a measuring lance or probe 11. A connecting lead 14 of platinum for the electrolyte 13 at the measuring lead 15 forms, together with a gaseous oxygen carrier 16 introduced from the top into the protective tube 12, a comparison electrode 14, 16 located in direct contact with the electrolyte 13. The measuring lead 15 actuates a potential measuring instrument 17 which in the present case is directly short-circuited with the molten metal 21, namely by way of support magnets 18 applied to the mould 19 forming the afore-mentioned metallurgical vessel.

Further details of the dip head screwed into the measuring lance 11 of Fig. 1 can be seen from Fig. 2. The protective tube 12, which consists usually of quartz, tapers towards the dip end, so that the electrolyte 13, which is constructed as a conical plug, remains projecting a predetermined distance from the protective tube 12. As its inside, the